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SHORT COMMUNICATIONS

Stress relaxation due to chain fractures in transient polymer networks

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Abstract: Aspects of a network model for concentrated dispersions are applied to polymer networks. It is shown how network deformation caused by network fracture affects the macroscopic stress.

Key words: Stress relaxation, polymer, transient-network theory

1. Introduction

The rheological behaviour of many concentrated polymer solutions and polymer melts is satisfactorily described by transient-network models [1]. Many of these models find their origin in the early transient-network theory, developed by Green and Tobolsky [2], Lodge [3] and Yamamoto [4]. Several modifications had to be introduced in order to obtain the abovementioned agreement with experimental data. These adjustments mostly concerned either network kinetics, i.e. the probability that chains become part of the network or become separated from it [5], or the relation between the deformation of the chains and macroscopic deformation [6, 7]. An explanation of the modification in terms of physical properties of the microstructure could not always be given. In this note such a modification, namely the one that is associated with the interplay between kinetic processes in the network and network deformation, is outlined and its consequences are displayed. The approach parallels the analysis of similar processes in a network of dispersed particles of colloidal dimensions [8].

2. Theory

The shear stress τ at time t of a material that has experienced an infinitesimal simple-shearing displacement γ_0 at time τ reads:

$$\tau(t) = \gamma_0 G(t-\tau), \tag{1}$$

where $G(t)$ is the relaxation function. Boltzmann's superposition principle can be applied when γ does not go beyond the range of linear mechanical response of the material:

$$\tau(t) = \int_{-\infty}^{t} \dot{\gamma}(\tau)\, G(t-\tau)\, d\tau. \tag{2}$$

Function $G(t)$ can be expressed in terms of network properties by means of an underlying transient-network model. In order to do so Kramers expression will be used for the macroscopic stress of an incompressible transient network; see [8] and [9]:

$$\boldsymbol{T}(t) = -p\,\mathbf{1} + \int_{-\infty}^{t} \int \boldsymbol{q}(\boldsymbol{q}', t' \mid t)\, \boldsymbol{f}(\boldsymbol{q})\, \Psi(\boldsymbol{q}', t' \mid t)\, d^3\boldsymbol{q}'\, dt', \tag{3}$$

where p is the ambient pressure, $\boldsymbol{q}$ the average chain vector at time t of chains created at time $t' \leqq t$ with chain vector $\boldsymbol{q}'$, $\boldsymbol{f}$ the force transmitted by a chain with chain vector $\boldsymbol{q}$, and $\Psi(\boldsymbol{q}', t' \mid t)\, d^3\boldsymbol{q}'\, dt'$ the concentration at time $t \geqq t'$ of chains that were created during the time interval $(t', t' + dt')$ within the configuration range $d^3\boldsymbol{q}'$ about $\boldsymbol{q}'$.

Though not explicity indicated $\boldsymbol{q}$ is actually a time average over a period that is large with respect to the time associated with thermal fluctuations and small with respect to the one associated with the rate of deformation (i.e. $\dot{\gamma}^{-1}$ in simple-shear flow). All chains have the same and constant probability, say $h\,dt'$ of leaving the network during the interval dt'. At the moment when chains are created they have the same distribution of lengths and orientations as a set of free

chains. We adopt a Gaussian distribution for them, so:

$$\Psi(\boldsymbol{q}', t' \mid t') = g \left(\frac{a}{2\pi kT}\right)^{3/2} \mathrm{e}^{-\frac{aq'^2}{2kT}}, \tag{4}$$

where g is the number of chains created per unit volume and unit time, k Boltzmann's constant, T the absolute temperature and a the force-law constant:

$$\boldsymbol{f} = a\,\boldsymbol{q}\,. \tag{5}$$

This is equivalent to the force law used in [8]:

$$\boldsymbol{f}(\boldsymbol{q}(\boldsymbol{q}', t' \mid t)) = \left(f(q') + c(q')\frac{q(q', t' \mid t) - q'}{q'}\right)\frac{\boldsymbol{q}(\boldsymbol{q}', t' \mid t)}{q(\boldsymbol{q}', t' \mid t)}, \tag{6}$$

if $f(q') = c(q') = a\,q'$. Note that for a freely jointed chain made up of $v-1$ links of length L, where $v \gg 1$:

$$a = \frac{3kT}{(v-1)L^2}. \tag{7}$$

The constancy of the annihilation function, h, implies that:

$$\Psi(\boldsymbol{q}', t' \mid t) = \Psi(\boldsymbol{q}', t' \mid t')\,\mathrm{e}^{-h(t-t')}. \tag{8}$$

In order to be able to perform the integrations involved in eq. (3) the $\boldsymbol{q}$-vector must be related to the applied deformation. In the case of affine deformation:

$$\boldsymbol{q}(\boldsymbol{q}', t' \mid t) = \boldsymbol{F}_{t'}(t) \cdot \boldsymbol{q}', \tag{9}$$

where $\boldsymbol{F}_{t'}(t) \equiv \dfrac{\partial \boldsymbol{x}(t)}{\partial \boldsymbol{x}(t')}$, the macroscopic relative deformation gradient ($\boldsymbol{x}(t')$ and $\boldsymbol{x}(t)$ denote the position vectors of the same material point at times t' and t respectively). Eqs. (4–9) are substituted in eq. (3) after which the integration over configuration space is performed. The result is:

$$\boldsymbol{T}(t) = -p\,\mathbf{1} + g\,kT \int_{-\infty}^{t} \boldsymbol{C}_t^{-1}(t')\,\mathrm{e}^{-h(t-t')}dt', \tag{10}$$

where $\boldsymbol{C}_t(t') \equiv \boldsymbol{F}_t^{\dagger}(t') \cdot \boldsymbol{F}_t(t')$, the relative Cauchy strain tensor. The relaxation function according to this expression becomes:

$$G(t) = n\,kT\,\mathrm{e}^{-th}, \tag{11}$$

where $n = g/h$ is the chain density which is a constant under these considerations. These familiar and simple results (see also [3]) are valid only when eq. (9) applies. However, in a previous paper [8] it was argued that instead of eq. (9) it is more realistic to write:

$$\boldsymbol{q}(\boldsymbol{q}', t' \mid t) = \tilde{\boldsymbol{F}}_{t'}(\boldsymbol{q}', t) \cdot \boldsymbol{q}', \tag{12}$$

where $\tilde{\boldsymbol{F}}$ is not necessarily equal to $\boldsymbol{F}$. This tensor follows from a more or less detailed study of contraction phenomena in networks of colloidal particles after fracture of force-carrying chains (see [8]). It is associated with the vector function $\boldsymbol{\chi}$, defined as:

$$\boldsymbol{\chi}(\boldsymbol{q}', t' \mid t) = (\boldsymbol{F}_{t'}(t) - \tilde{\boldsymbol{F}}_{t'}(\boldsymbol{q}', t)) \cdot \boldsymbol{q}'. \tag{13}$$

Figure 1 illustrates that $\boldsymbol{\chi}$ indicates how much the fracture of chains causes the chain deformation to remain behind with respect to the macroscopic deformation.

In [8] it has been argued that:

1) $\chi \sim q'$,
2) $\boldsymbol{\chi} \parallel \boldsymbol{q}$.

This implies that reorientation of chains after fracture is not taken into account in these considerations.

3) in the case of a stepwise deformation at time t'':

$\chi \sim$ the fraction of those chains present at time t'' that are no longer present at time t,
$\chi \sim$ the excess chain force at time t transmitted by a chain created at time t', where $t' \leqq t'' \leqq t$.

Again in the case of a stepwise deformation at time t'' it follows that:

$$\boldsymbol{\chi}_{t''}(\boldsymbol{q}', t' \mid t) = \lambda q'(1 - \mathrm{e}^{-h(t-t'')}) \cdot (f(\boldsymbol{q}(q', t' \mid t)) - f(\boldsymbol{q}'))\frac{\boldsymbol{q}(\boldsymbol{q}', t' \mid t)}{q(\boldsymbol{q}', t' \mid t)}. \tag{14}$$

The extra subscript t'' denotes that $\boldsymbol{\chi}$ (and thus $\tilde{\boldsymbol{F}}$) are also related to the deformation gradient, i.e. the time at which the step deformation takes place. Further λ is a proportionality factor [$\mathrm{kg}^{-1}\,\mathrm{m}^{-1}\,\mathrm{s}^2$] which will be evaluated later on. The term with the exponent denotes the fraction of the chains that have broken between t'' and

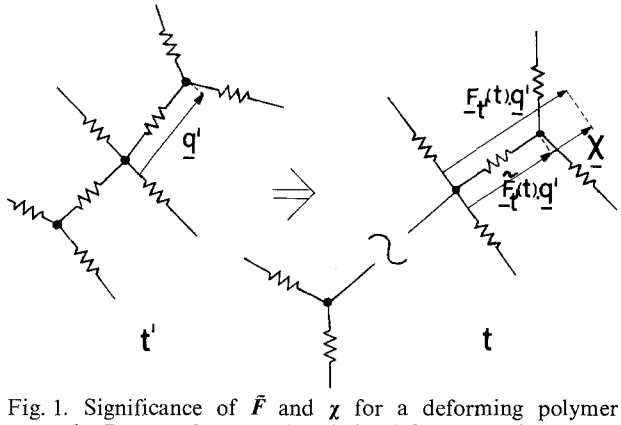

Fig. 1. Significance of $\tilde{\boldsymbol{F}}$ and $\boldsymbol{\chi}$ for a deforming polymer network. Due to fracture the chain deformation is seen to remain behind with respect to the macroscopic deformation

t. From eqs. (5), (13) and (14) it follows that:

$$\tilde{\boldsymbol{F}}_{t',t''}(\boldsymbol{q}',t)=\frac{1+\Lambda\dfrac{q'}{|\boldsymbol{F}_{t'}(t)\cdot\boldsymbol{q}'|}(1-\mathrm{e}^{-h(t-t'')})}{1+\Lambda\,(1-\mathrm{e}^{-h(t-t'')})}\boldsymbol{F}_{t'}(t)\,, \tag{15}$$

where $\Lambda\equiv\lambda a q'$. Each of the expressions (14) and (15) show that there is affinity of the chain deformation with the macroscopic deformation if $\lambda=0$, i.e. $\Lambda=0$. This corresponds to the assumptions made in the early transient-network theories. In the limit $\lambda\to\infty$, i.e. $\Lambda\to\infty$, chains adopt the lengths at which they were created. It should be noted that expression (15) is equivalent to expression (37) in [8] for one chain complexity and $c=aq'$. The relaxation function corresponding to eq. (10) after substitution of eqs. (4–6), (8) and (12), i.e. $\boldsymbol{C}_t(t')$ is replaced by $\tilde{\boldsymbol{C}}_{t,t''}(t')=\tilde{\boldsymbol{F}}^{\dagger}_{t,t''}(t')\cdot\tilde{\boldsymbol{F}}_{t,t''}(t')$ with $t''=0$, has been shown to read (eq. (55) in [8]):

$$G(t)=\frac{\mathrm{e}^{-ht}}{15}\int_0^{\infty}q'\,(3aq'+2A(q',t))\,N_{\mathrm{init}}(q')\,dq'\,, \tag{16}$$

where

$$A(q',t)=\frac{aq'}{1+\Lambda\,(1-\mathrm{e}^{-ht})}\,, \tag{17}$$

and

$$N_{\mathrm{init}}(q')=4\pi q'^{2}n_0\left(\frac{a}{2\pi kT}\right)^{3/2}\mathrm{e}^{-\frac{aq'^{2}}{2kT}}\,, \tag{18}$$

the density of chains of length q' in the initial state.

It has been argued in [10] that a realistic value of Λ ($=\lambda a q'$) will be unity (i.e. a constant). Since for Gaussian springs a is constant (see eq. (7)), this implies that $\lambda\sim q'^{-1}$. So for this particular system it seems to be rational to replace the term $\lambda q'$ in eq. (14) by Λ/a. It should be noted here that expression (14) has basically been postulated for colloidal networks, and that the significance of λ needs reconsideration when contraction phenomena in other systems are described with it. When Λ is a constant the integration in eq. (16) can be performed analytically. The result can be written as a series:

$$G(t)=\sum_i G_i\,\mathrm{e}^{-t/t_i}\,, \tag{19}$$

where G_i is the strength of the mechanism with relaxation time τ_i. When $\Lambda=0$, so that $A(q',t)$ in eq. (16) equals c ($=aq'$), the resulting expression is identical to the one that follows from the early transient-network theory:

$$\tau_1=1/h\,,\qquad G_i=\begin{cases}n_0kT & \text{if } i=1\,,\\ 0 & \text{if } i>1\,.\end{cases} \tag{20}$$

When Λ is larger than zero but a constant, the integration in eq. (16) can be carried out to give:

$$\tau_i=1/ih\,,\qquad G_i=\begin{cases}\dfrac{n_0kT}{5}\left(3+\dfrac{2}{1+\Lambda}\right) & \text{if } i=1\,,\\[2ex] \dfrac{2n_0kT}{5\,(1+\Lambda)}\left(\dfrac{\Lambda}{1+\Lambda}\right)^{i-1} & \text{if } i>1\,.\end{cases} \tag{21}$$

$A(t)$ has first been written as a series in order to obtain this result.

When $\Lambda\cong 1$ the strengths for $i>1$ cannot be disregarded with respect to the one for $i=1$, so that the incorporation of contraction phenomena leads to a considerable modification of the stress, i.e. expression (21) then differs considerably from expression (20) that corresponds to the early network theory. With Λ increasing, the strength of the longest apparent relaxation mechanism becomes smaller. We call them *apparent* mechanisms here, because they are all related to one and the same structural effect namely the contraction given by eq. (14) and illustrated in figure 1. The sum of the strengths is a constant:

$$\sum_i G_i=n_0kT\,. \tag{22}$$

The mechanism that leads to the relaxation spectrum (21) instead of (20) may be important for the interpretation of the relaxational behaviour of concentrated polymer solutions and melts. This spectrum will arise even if there is no need to distinguish between different types (complexities) of segments. The effect of the contraction phenomena on the linear viscoelastic response in shear experiments other than the instantaneous displacement is given by eq. (2) on substitution of eqs. (19) and (20) or (21).

3. Discussion

Several assumptions that underly the concept of interplay between kinetic processes taking place in networks and their state of deformation have been extensively discussed elsewhere [8], and their validity will not be discussed here. An exception will be made for the consequences of the Gaussian character of the chains representing the molecules. Eq. (14) was based on the idea that the contraction of a certain chain of colloidal particles after fracture of any chain elsewhere is, amongst other things, proportional to the extra force that this specific chain carries with respect to the force it carried at the moment of its creation. Though it

cannot be easily checked if this specific assumption holds for polymeric systems, there seems to be no doubt that there will be a network displacement after fracture and that eq. (14) qualitatively accounts for this effect.

The extension to more complicated networks consisting of chains with a number of complexities (which have, for instance, another value of h) can be easily made when the kinetic processes that take place in network chains of different complexities do not influence each other. As a result of this spectra (20) and (21) of each such mechanism may be summed in order to obtain the spectrum of the total system. It should be noted that in [8] the model is extended so far that such an independence does not hold.

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